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# **OXIDATION UNSUSCEPTIBLE PHOTOCATHODES FOR NEAR-UV**

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A thesis submitted to the University of Huddersfield in partial fulfilment of the requirements for the  
degree of Master of Science

The University of Huddersfield (in collaboration with – Orion Engineering Ltd)

Submission date as April 2020

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## **Abstract**

The overall aim is to identify a suitable material for photocathodes that produces a sufficiently high flow of electrons, despite limited oxidation during operational life in low vacuum. The most promising strategies and materials were investigated. The strategy was, to use elements/alloys and their oxides that have a suitable UV LED emission work function and use an alloy with a low work function element. The materials selected for study were aluminium alloy 2014, aluminium alloy 2060, manganese, silver and pure titanium. Magnetron sputtering was used to create the thin films of materials for study. The photoelectron current generated when UV light was shone on the film was measured and recorded over 24 h in high and low vacuum. In conclusion, Mn and alloy 2014 produced poor results, alloy 2060 was an improvement, but did not produce a high enough photocurrent until more silver was added. Pure titanium results were similar to alloy 2014. Other options such as nitride film and nickel were tested with little positive results. Recommendations are to explore alloy 2060 with more silver and titanium, look at copper, silver and investigate nitride films further.

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## **Introduction**

We have recently developed a significant interest in instrumentation where a progressively oxidised photocathode will need to perform with defined efficiency, which can be set at a few nA of current, reliably and as long as possible between cleaning, during use in a relatively low vacuum environment.

This study is a logical extension to the main, company initiated project and is designed to refine the photocathode material used in the main project. Up to now all the data published is for high or ultrahigh vacuum. This mostly dictated by the fact that the surface state affects photocathode quantum efficiency very significantly and surface oxidation leads to photocurrent reduction by various fundamental processes.

There is little or no data apparent on low vacuum photocathode performance. The data for photocathodes with partially oxidised surfaces also does not appear in many publications.

### **Aim of the project:**

The overall aim is to identify a suitable material for photocathodes that produces a sufficiently high flow of electrons with limited oxidation during operational life. This was achieved by a number of objectives:-

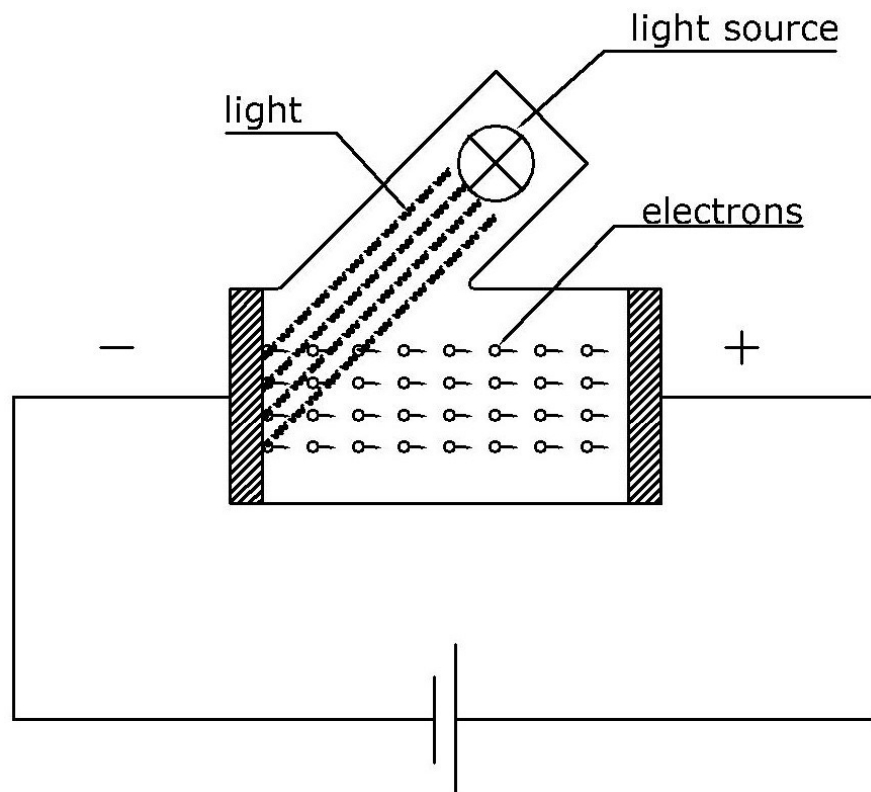
1. Specify the photo cathode operating conditions.
2. Identify the most promising materials, processes and strategies.
3. To investigate the photo emissivity of the chosen materials.
4. Analyse the results and recommend areas for future work.

# Chapter 1 Photocathode Operating Conditions

## 1.1 Background and General Theory

Photoemission is well known and studied process. Hertz first observed the effect in 1887. It was subsequently investigated by Thompson and Lenard, with the theory being provided by Einstein in 1905 (B. Feuerbacher, 1978, p. 1).

The photoelectrical effect can be observed when two electrodes (plates) are placed in a vacuum sealed container and a light is shone on the (negative) electrode, causing electrons to escape to the vacuum and flow to the (positive - anode) plate, as illustrated below. The electron current depends on light wavelength (photon energy), light flux (intensity) and the cathode material properties, which includes work function and electron densities of state, to name a few. The basic principle of operation is presented at Fig.1.



$$E = hf - \phi$$

**Figure 1 Illustration of the Photo Electric Effect**

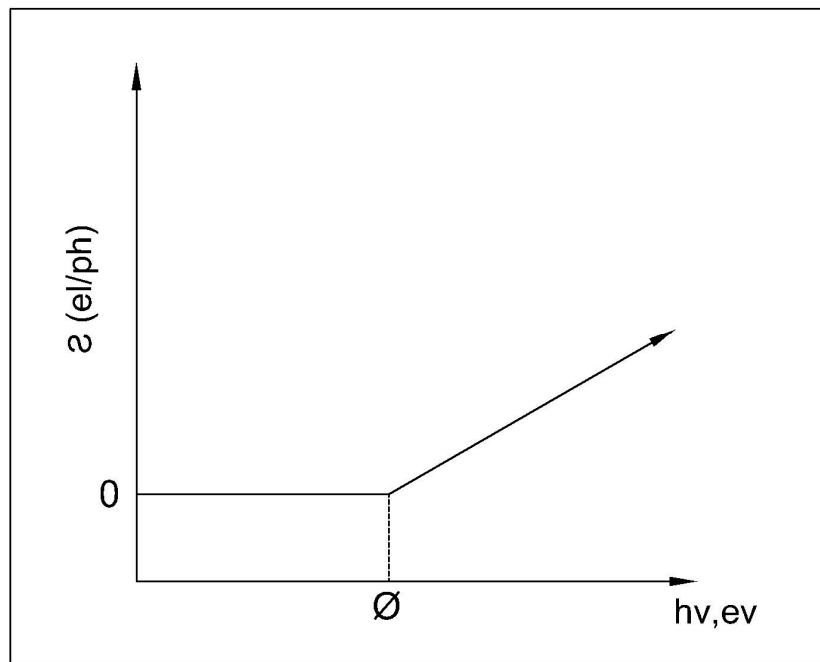
The formula arrived at by Einstein from the experimental work done, is that the maximum kinetic energy of electrons equals Plank's constant multiplied by the light frequency, less the work function and is shown above (B. Feuerbacher, 1978, p. 1).

It was also realised by researchers' that the wavelength of light was also important. Below a certain wavelength (threshold wavelength) a metal would not emit electrons. The work function refers to the



minimal light energy at which photoelectrons will be emitted (see Fig.2). The quantum efficiency ( $\eta$ ) is a number of photoelectrons emitted for each photon. At the photon energy below the work function we would have zero efficiency, above the work function energy, the efficiency increases with the growth of light energy as shown.

The conclusion we arrive at this point is that the light source should have the highest possible energy (the shortest wavelengths). The most economical way is to use Light Emitting Diodes (LEDs) as a light source. The light intensity matters as well, after all more photons with the right energy will create more electrons. The most economical and widely available LED has the wavelength of 278 nm or energy of at around 4.5 eV. The LED sources are discussed below.



**Figure 2 Schematic Representation of the Photo Effect Quantum Efficiency on Photon Energy**

It appears that many elements have a work function value low enough for our LED to produce photoelectrons. In this case the basic processes can be presented as in Fig 2.

**Table 1 Properties of Various Elements**

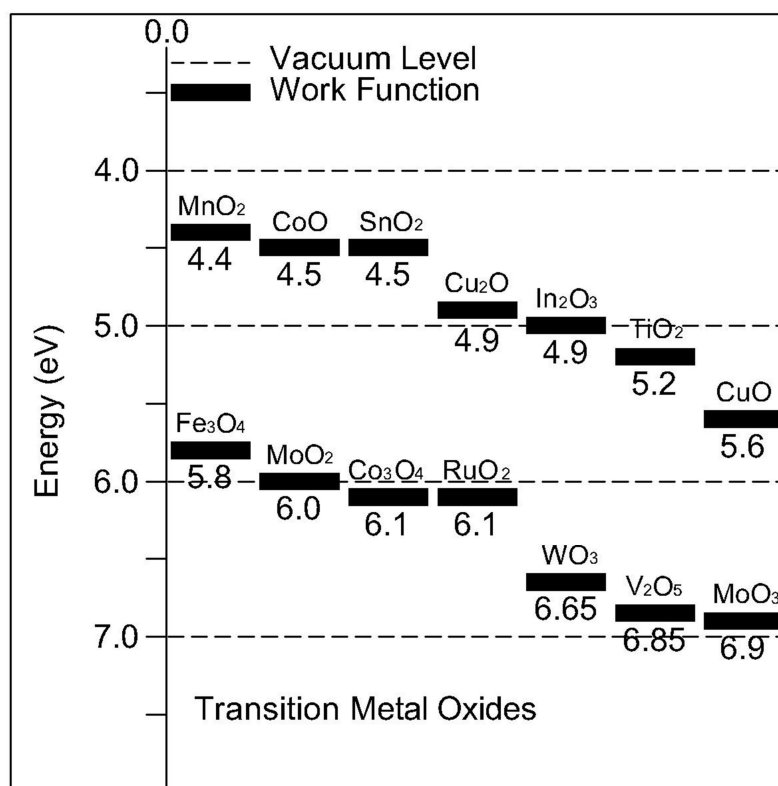
Atomic number (Z)	Symbol	Name	Structure type	Electro negativity	Work Function (eV)	Threshold Wavelength (nm)	Resistance $\mu$ ohm cm
3	Li	Lithium	bcc	1.0	2.4	517	9.47
6	C	Carbon	hex	2.5	4.7	264	10
12	Mg	Magnesium	hcp	1.2	3.6	344	4.48
13	Al	Aluminium	fcc	1.5	4.25	292	2.66
14	Si	Silicon	diamond	1.8	4.8	258	48
22	Ti	Titanium	hcp	1.6	3.95	314	42
25	Mn	Manganese	bcc	1.5	3.8	326	185
26	Fe	Iron	bcc	1.7	4.3	288	9.71
28	Ni	Nickel	fcc	1.8	4.5	276	6.84
29	Cu	Copper	fcc	1.9	4.4	282	1.673
30	Zn	Zinc	hex	1.5	4.2	295	5.8
37	Rb	Rubidium	bcc	0.8	2.2	564	13.1
47	Ag	Silver	fcc	1.8	4.3	288	1.59
55	Cs	Caesium	bcc	0.8	1.8	689	20.8
56	Ba	Barium	bcc	0.9	2.5	496	34
74	W	Tungsten	bcc	1.9	4.5	276	5
78	Pt	Platinum	fcc	2.1	5.3	234	9.85
79	Au	Gold	fcc	2.3	4.3	288	2.35
Where $E = hf - \phi$ $E = \phi = hc/\lambda$ , so $\lambda = hc/\phi$							
E = Energy, h = Planck's Constant, c = speed of light, $\lambda$ = wavelength,							
Note :- Data from A. Earnshaw, Norman Greenwood, Chemistry of the Elements							
Note :- Data from M. Cardona and L. Ley front cover of Topics in Applied Physics, Photoemission in Solids 1 (work function & electronegativity).							
hc source & all formulae, Elert G., The Physics Hypertext Book							

The single metal/element work functions are listed in Table 1. It can be seen that the very low work function (at around 2 eV) is only observed for alkali metals. Alkali metals are very active chemically and very difficult to handle, with a high oxidation rate. Most conventional bulbs, like incandescent or halogen bulbs do not provide photons with enough energy required to excite the electrons from a stable metal. A low wavelength (UV) light is required. This can be obtained economically from an UV LED. Some examples of available LEDs are shown in Table 2. The LG LED at the beginning of the project was almost £300. As the LEDs development continues the price dropped to below £50. The LG LED was chosen for the project. As the LED has to operate in vacuum, heat dissipation was a potential problem, the LED power was limited to 20% from nominal 2 mW.

**Table 2 Relationship between Photon Energy and Price**

Component No.	Wavelength (nm)	Photon energy (eV)	Light Output (mW)	Cost Each £	Comments	Source
LEUVA66B00HF00 LG	278	4.46	2	42.76		rs-online.com
S-T39B-B1-275-01	278	4.46	0.9	400.0		Anderton's distributor
1920890	355	3.49	0.3	36.28	minimum order 1000+	farnell.com
1920892	377	3.29	1.3	15.03		farnell.com
888-7319	420	2.95	6	11.95		rs-online.com

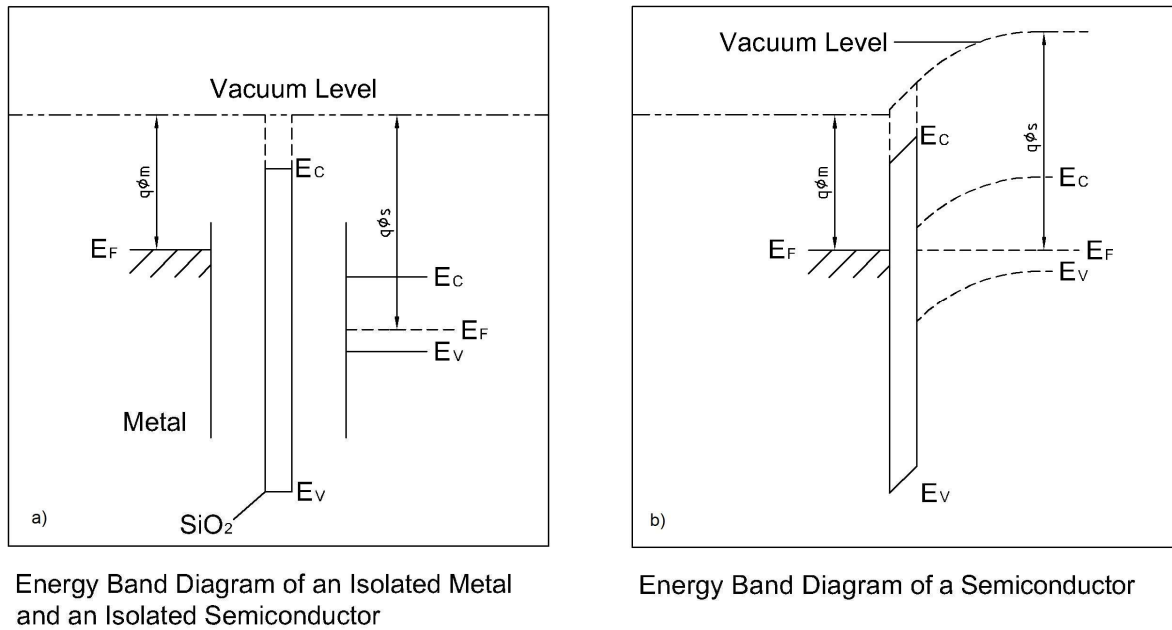
The photocathode will oxidise in a working vacuum and we need to have a look at the work function of oxides. Some known values are presented in Fig.3.



Source: Wiley-VCH Verlag GMBH & KGaA  
Royal Society of Chemistry

**Figure 3 Some Work Function Values of Oxides**

It looks like Mn can be a good candidate for the photocathode as both the work functions for the metal (3.8 eV from Table 1) and the oxide (4.4 eV from Fig 3) are below the energy of chosen LED light (4.5 eV from Table 2). There are two energy diagrams can be drawn for the photoemission process. For the pure metallic surface, or for a free-standing semiconductor (SiO<sub>2</sub> in this case) the diagram can be presented as in Fig. 4a. The work function in this case is defined by moving an electron from the collective states into the vacuum levels in a straightforward manner. When oxide grows on a metal (Fig 4b), the picture gets more complicated as the two substances are joined by the Fermi level (Cardona, et al., 1978, p. 17). Electrons can be excited in the metal and (if semiconductor is thin enough) tunnel through the semiconductor and escape to vacuum (work function allowing) or be excited in the oxide (semiconductor) and leave the material (work function limitation still applies). The presence of dopants can shift the Fermi level in the semiconductor towards the conduction zone and thus lower work function for the electrons excited in the metal, which then tunnel through the semiconductor.



**Figure 4 Energy Diagrams for Free Standing Metal and Oxide -a) and -b) Contact (film on metal) Metal-Oxide)**  
Source <https://physics.stackexchange.com>

## 1.2 Defining Photo Cathode Operating Conditions

From a semantic point of view, the photoelectric effect can be, as a very simple model, described as a three step process (Cardona, et al., 1978, p. 190) :-

1. The process starts by a photon striking the surface of an element and having enough energy to excite an electron and start it on it's journey.
2. The electron moves towards the surface.
3. Having enough energy, the electron leaves the surface completing the process.

After metal deposition we start emission from the almost pure metal surface. The current will be at the high level if the LED source has enough energy to send electrons to the vacuum level. As we did not have so high a vacuum, the oxide would start growing on the surface and we would have “mixed” photoemission from the metal (electrons should travel through the oxide) and oxide itself. As the oxide growth increases, the emission from the metal will significantly diminish and the main process will be from the oxide.

The aim of this work is to find an oxide or oxide doped metal to enhance the photoemission of the metals. This proves challenging within the limited timeline of this project, due to lack of the in depth study of the phenomenon under low vacuum in the literature.

### **1.3 The Effects of External Factors on the Surface**

Usually, to stop impurities from contaminating the surface of a sample and to get reliable (stable and consistent) results, most of the photoemission applications use a high vacuum above  $10^{-8}$  Torr. Our interest lies instead in a vacuum lower than  $10^{-2}$  Torr. This will lead to rapid surface oxidation and we will need to rely onto metal/oxide photoemission for the functionality of the emitter for a relatively stable and high enough (few nA) current.

#### **1.3.1 The Presence of Oxygen**

As surface oxidises in the low vacuum, the photocurrent will decline slowly. In part this is due to the lower quantum efficiency of oxide photo emission (Fig 3). It is impossible to make predictions of a general nature as the processes are very complex, almost not scientifically understood and need very detailed analysis, which is outside the scope of this work. If the oxide has a high value of work function (higher than LED light energy), then emission will decline to zero. If the oxide has a lower work function value, then there is a hope of some photoemission. The best scenario is if the material oxidises only with a thin, electron partially transparent oxide and some impurities (we can say also dopants), that will keep the Fermi level high enough to provide emission from the underlying metal and the oxide itself.

## **Chapter 2 Identify Strategies Used**

### **2.1 Identify Materials and Strategies**

There may be some of strategies that can be employed to minimise and utilise the effects of oxidation.

#### **2.1.1 Alloy Elements that have little Interaction with Oxygen**

The first strategy would be to use an element that does not have much interaction with oxygen such as silver. However, the downside of this approach is that the work function value of silver is high. Silver does form compounds which are unstable, so care has to be taken, although it's resistance to oxidation is well documented (M. Boccas, 2006).

Aluminium reacts rapidly with oxygen and instantly forms a film, but is relatively cheap and alloys easily. In aluminium alloy 2014, it is alloyed with primarily with copper, 3.9 to 5%, manganese and magnesium in lower quantities. Curiously, this alloy does not anodise, so the copper content has a substantial effect and may have an interesting response to the ultra-violet light.

#### **2.1.2 Alloy a Low Work Function Element**

Another option is to ensure that a low work function element is part of an alloy. The idea being that the incorporation of a low work function element into an alloy will give the benefit of enhanced emission, while using the alloy properties to counter or use oxidation to advantage and suppress other undesirable effects. Alloy 2060, is a similar alloy to 2014, with the same amount of copper but also has lithium added. This is an alloy of interest to the study, as lithium is a low work function element and its presence may give a strong emission response (Cardona, et al., 1978, p. front cover).

Aluminium could be replaced by magnesium as the bulk element in an alloy, as the work function value of magnesium is significantly lower than aluminium as shown in Table 1. Magnesium alloys may be an option, however these usually alloy with significant amounts of zinc, which is not the best element to use in vacuum systems. There are other magnesium alloys which use rare earth elements, but would gain little in reducing the work function value. The ideal alloy from a work function point of view would be a magnesium, aluminium, lithium alloy. These alloys do exist, but they do not appear to be commercially easily available (R. Wu, 2015, pp. 65 - 100).

Like aluminium, titanium is another element that has high affinity for oxygen (Greenwood & Earnshaw, 1998, p. 958), so much so that it is used as an absorber in ion or 'getter' pumps (Mattox, 2010, p. 119). It should produce photoelectrons under our chosen LED source as indicated in Table 1. It is sensitive to trace amounts of oxygen, nitrogen and carbon, which allows for the possibility of nitride and carbide coatings, and does alloy readily with other metals (Greenwood & Earnshaw, 1998, pp. 957 - 959).

### **2.1.3 Coat a Material with a low Work Function Element**

Another option would be to completely coat the surface of an element with a material of low work function. For example, it was found that when tungsten wire was coated completely with caesium, the tungsten wire took on the work function value of caesium (Cardona, et al., Photo Emission in Solids 1, 1978, p. 5). While caesium is not suitable for use on safety grounds, other coating materials could be utilised that exclude oxygen.

Looking at nitrides, they have also been known to produce relatively high photocurrent and have relatively low work function (Funakawa, Yamamuro, Luo, & Sugino, 2004, pp. 994 - 998). The coatings are also durable. However, the nitride system behaviour is quite dependent on nitrogen content and it was difficult to study sensibly in this work.

Diamond like carbon DLC, has useful emission properties (Mattox, 2010, p. 387). Work has also been done on DLC (Xu & Huq, 2005, pp. 72 - 73). The properties of the film can vary according to which process and the parameters (Leal, Fraga, A., Sobrinho, & Massi, 2015). DLC would also be a hard-wearing film.

### **2.1.4 Combination Option**

The final strategy would be a combination of the options discussed above. A rough surface finish could also be employed where appropriate on the photo cathode, dependant on the material used, to help facilitate electron emission, but would need to be additionally studied for oxidation effects (Xue, 2013, pp. 1 - 5) (Xue, 2017, pp. 903 - 907).

## 2.2 Overview of the Experiment

To deposit thin films under various operating conditions, magnetron sputtering techniques have been used. The substrate samples (predominantly silicon) were placed in a vacuum chamber evacuated to the base pressure of  $10^{-1}$  Torr prior to film deposition. By combining materials as the magnetron target, this also gives the opportunity to create thin films of alloys which are not commercially available.

A cut away diagram of the experiment is shown below (Fig 5). Note, it is shown in the LED measurement position.

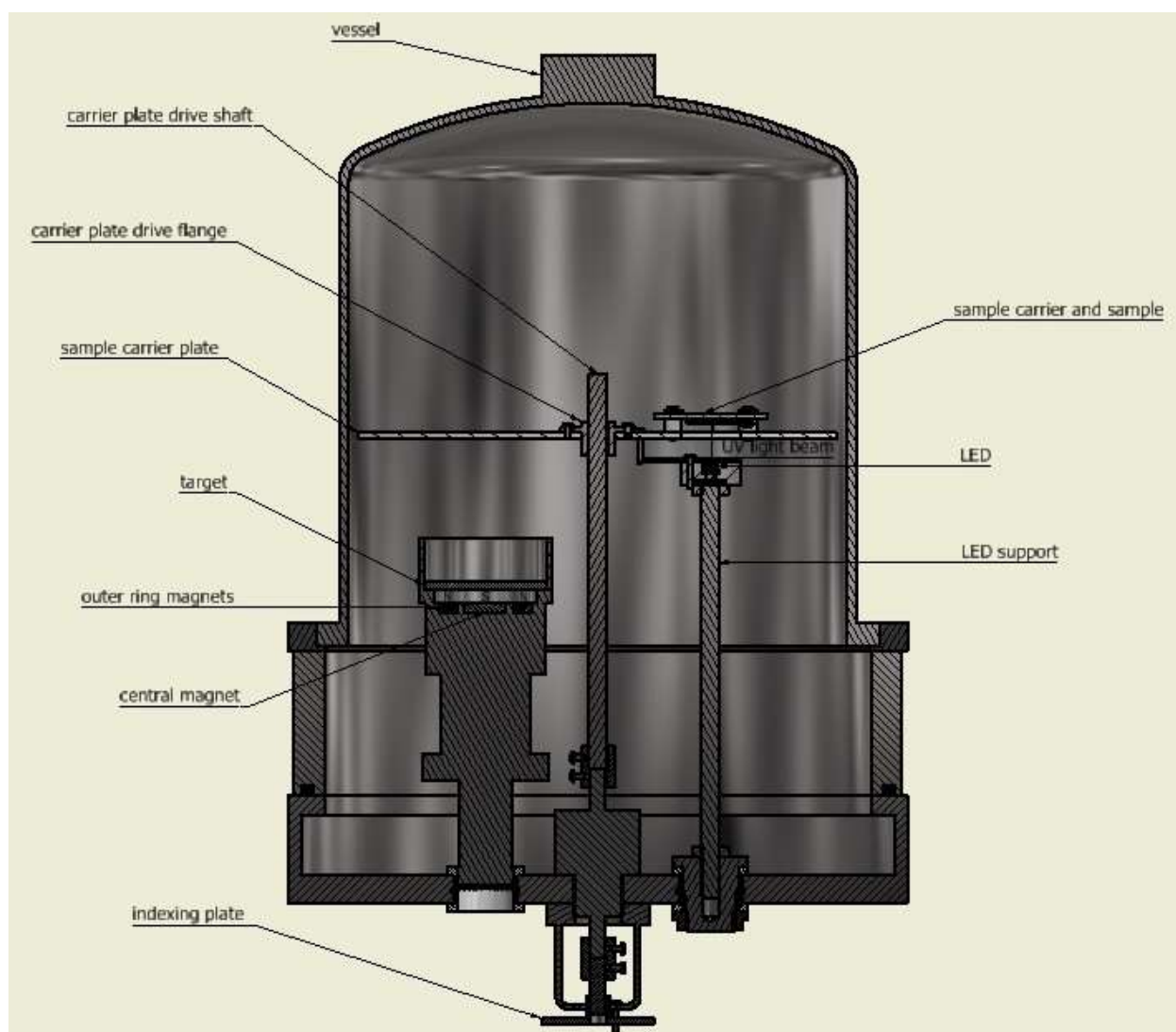
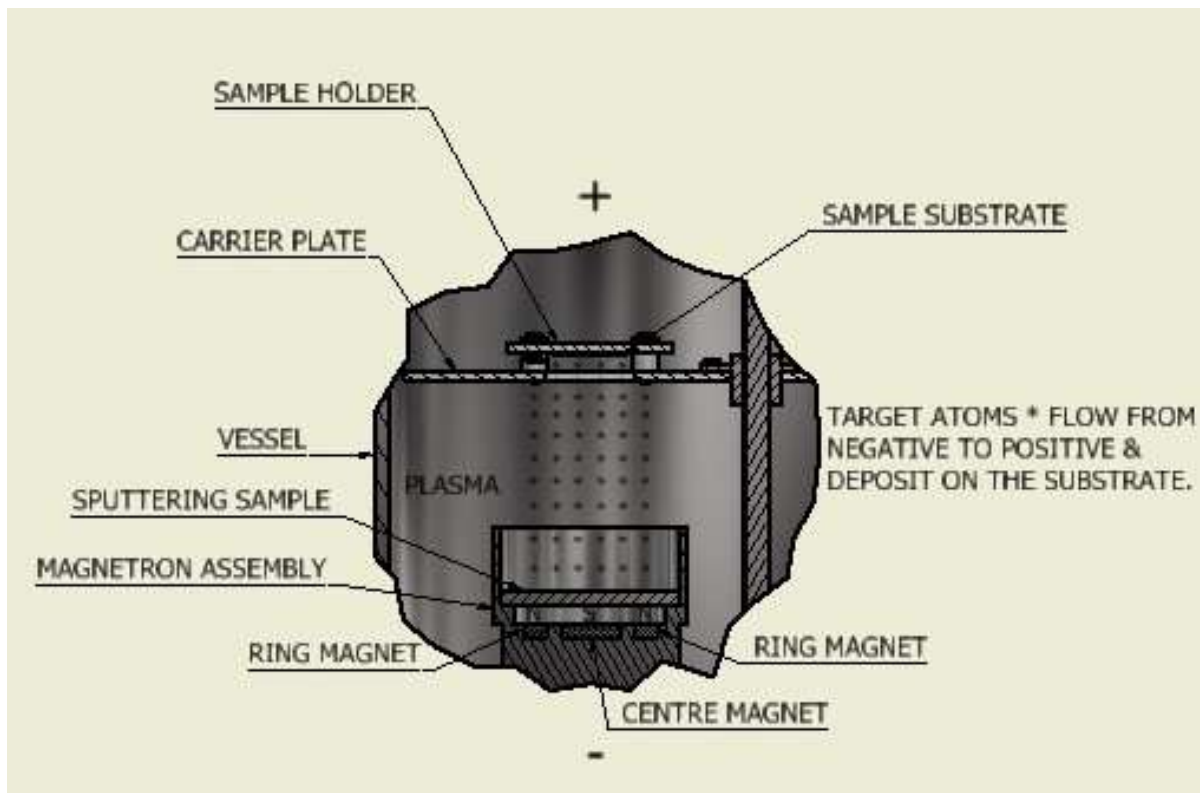


Figure 5 Cutaway Diagram of the Experiment

## 2.3 Description of the Experiment and Procedure

A silicon wafer sample was placed on a rotatable substrate holder mounted above the magnetron to allow sputter deposition of the coating material.

Once the desired vacuum has been obtained, gas, usually argon is fed into the chamber, so that the vacuum is maintained at  $10^{-1}$  Torr. In the majority of runs, listed in Table 3 below, the deposition was not reactive, so the gas flow was not measured. Once conditions are stable, the magnetron is started and the substrate will be sputtered with a target element/alloy of interest as illustrated below.



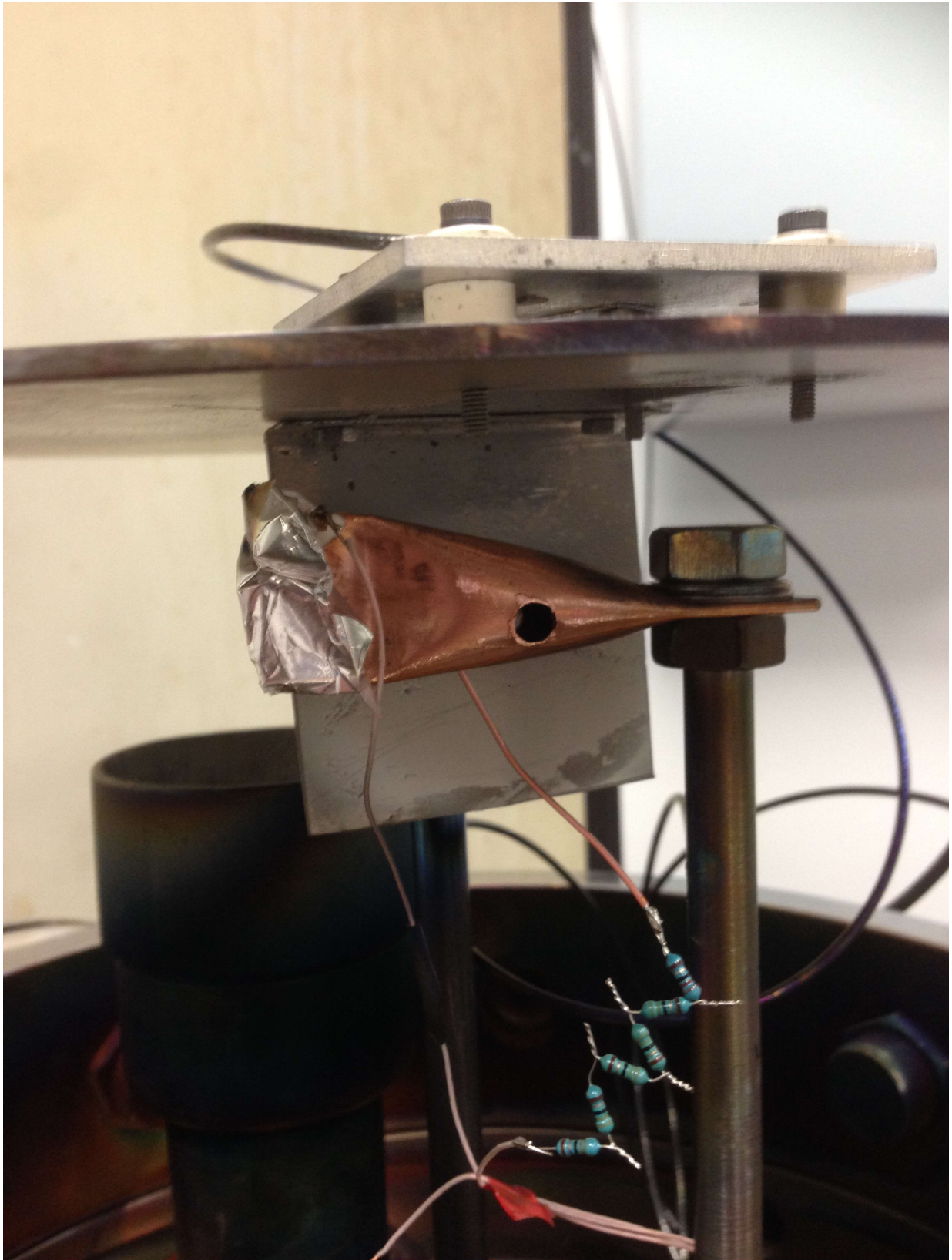
**Figure 6 Illustration of the Sputtering Process**

The sample is then indexed and a beam UV light shone onto the sputtered surface for a fixed time period on and off. The current generated is measured and recorded as discussed later.

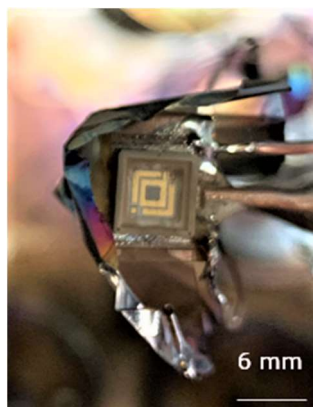
Mounting the LED presented a challenge, particularly after the original LED mounted in a metal can failed. A surface mount LED was procured and mounted as illustrated in the two photographs below.

The photograph (see Fig. 7) shows the LED mounting on a piece of copper tube (as a heatsink) shaped to mount the LED on and bolt on to the support. The photograph also shows the sample carrier plate and sample carrier, resistors for the LED, with the magnetron in the background. The aluminium foil surrounding the LED protects it from deposition when sputtering. A close up photograph of the LED is also shown below (see Fig 8). The grey square in the centre is the LED and to give some idea of size, it is approximately 2 mm square.





**Figure 7 LED Mounting**



**Figure 8 Close Up of the LED**

To clean the magnetron target, the procedure is to position the sample carrier away from the magnetron and deposit onto the sample carrier plate. The cleaning time is at around 10 min. Then the film is deposited when the silicon (in the sample carrier) is placed over the magnetron. The emission is measured when the plate is indexed over the LED and after the magnetron has been switched off.

## **2.4 Experimental Procedure – Material Selection**

### **2.4.1 Aluminium 2014**

This alloy has 3.9 to 5% copper. As copper is an element which has less interaction with oxygen, it would be expected to enhance corrosion resistance. The fact that the alloy will not anodise does suggest the interaction with oxygen is different from pure aluminium and other aluminium alloys.

### **2.4.2 Aluminium 2060**

Essentially the same alloy as above, but with the addition of 0.6 to 0.9% of lithium, along with very small additions of manganese, magnesium, silver and zirconium. The main interest for this study is that lithium is one of the lowest low work function elements, so it will be interesting to see how a low work function metal, alloyed as an element in aluminium which only forms a very thin stable oxide film, performs.

### **2.4.3 Titanium**

As discussed above, titanium forms an instant oxide film in the same manner as aluminium. It is also sensitive to carbon, nitrogen and UV light as indicated in Table 1.

## **2.5 Experimental Procedure – Gas Selection**

### **2.5.1 Argon**

The default gas for most experiments. Totally inert and does not react with any of the metals selected. This is ideal for sputtering a layer of the target as it is, with only any impurities in the chamber onto the substrate.

## 2.5.2 Nitrogen

Nitrogen does chemically react to form nitrides with the all mentioned metals. It was only used to create titanium nitride. Of particular interest given its other properties, is titanium nitride as recent work indicates a work function value of 4.2 to 4.5 eV (L.P.B. Lima, 2012, p. 86). Future work could also look at aluminium nitride, as recent work indicates a work function of 3.3 eV, but using deposition onto a heated substrate (A. Mezzi, 2018, p. 1138).

## 2.6 Experimental Procedure - Thin Film Deposition Conditions

Listed in the table below are the conditions for all the experiments run and recorded.

Sample No.	Material	Sputtering Time min	Voltage V	Power W	Initial Pressure Torr	Sputtering Pressure Torr	Measurement Pressure Torr	Plasma Gas Used	Gas Pressure Torr
1	Aluminium 2014	1	311	106	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
2	Aluminium 2014	5	400	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
3a	Pure Titanium	15	380	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
3b	Pure Titanium	15	380	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
4	Pure Titanium	15	632	100	$10^{-4}$	$10^{-1}$	$10^{-5}$	N	750
5	Pure Titanium	15	330	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
6	Pure Titanium	15	382	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
7	Pure Titanium	15	500	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	N	750
8	Aluminium 2060	15	361	100	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
9	Pure Titanium, then Aluminium 2060	2 & 5		200	$10^{-4}$	1	$10^{-4}$	Ar	1125
10	Aluminium 2060	5	363	94	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
11	Aluminium 2060	5	363	95	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
12	Aluminium 2060 + Ag	5	363	94	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
13	Aluminium 2060 + Ag	5	363	94	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125
14	50% Aluminium 2060 + 50% Mn powder.	5	200	120	$10^{-4}$	$10^{-1}$	$10^{-4}$	Ar	1125

**Table 3 Sputtering Conditions**

The deposition conditions and measuring procedures evolved as experience was gained creating the samples. The deposition pressure of the gas used was always the minimum to sustain stable magnetron operation. The voltage and power used were kept as consistent as practicable to maintain sputtering. Target cleaning time was 10 minutes, prior to the substrate being placed over the magnetron.

The sputtering time was varied to see what effect that would have on the results. After sample 9 the sputtering time was kept at five minutes. It was established that this has produced films of approximately 1 micrometre thickness. The limited time of the MSc course did not allow for measurement of the film thicknesses for all the samples to be carried out. It was therefore assumed that the influence of the film thickness on photoemission was negligible after a continuous film was established.

As discussed earlier, the process of photo emission from thin films covered by an oxide layer makes the process more complicated. It was essential to establish an LED irradiation protocol to obtain a consistent photoemission reading. It was also important to observe strict timing for how long the sample was illuminated, when the current reading was taken, and be consistent when taking readings. The current reading was taken on two minutes, just before switching off the LED. The exposure of the samples to the LED was varied on sample 3A. This was investigated when predictable anomalies occurred in the data. It was established that consistent and stable results were produced with two minutes LED on, one minute LED off for all samples.

Due to an equipment issue the voltage could not be recorded for sample 9, so the voltage column in Table 3 is left blank for that sample.

From sample 10 onwards, more than one film was deposited with the same composition. Some samples had elements added to observe the effect. It was done to check on whether the rate of emission decline varied, and a reading was also taken after 24 hours.

Samples were also partially exposed to air to see what effect that would have on the emission from the sample and the longevity of emission. With sample 13, after 24 hours it was completely exposed to air for two hours and then the emission was checked again.

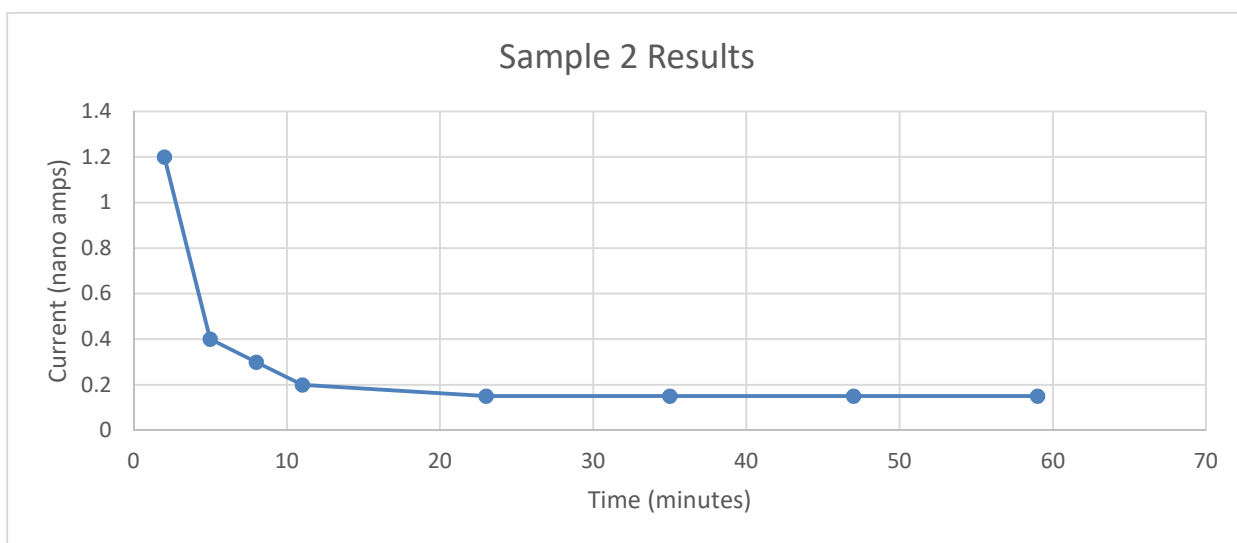
In some of the samples, various fleeting anomalies such as the meter not reading zero when the LED is switched off and brief instances of reversed polarity were observed and noted. Although the equipment appeared to be working normally, the only way to check was to repeat the experiment with another sample under the same deposition conditions. Then observe the results and see if the anomaly appeared again.

## Chapter 3 Results

The results for various samples are presented below describing the run conditions and data of the photocurrent vs time in vacuum. The experience gained from carrying out the experiments on various samples is discussed in the following sections. This also includes test runs that did not give a photoemission response.

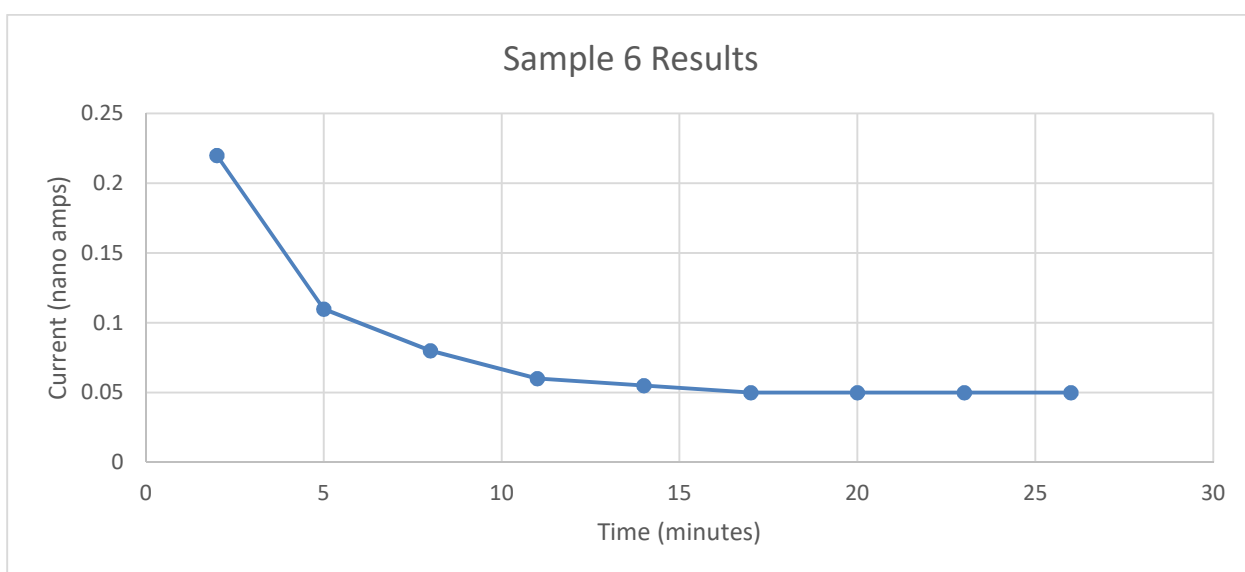
### 3.1 Observational Results

The results for deposited aluminium alloy 2014 are displayed below. Deposition was carried out for 5 minutes (Fig 9).



**Figure 9 Sample 2 Results, from Aluminium Alloy 2014 Thin film**

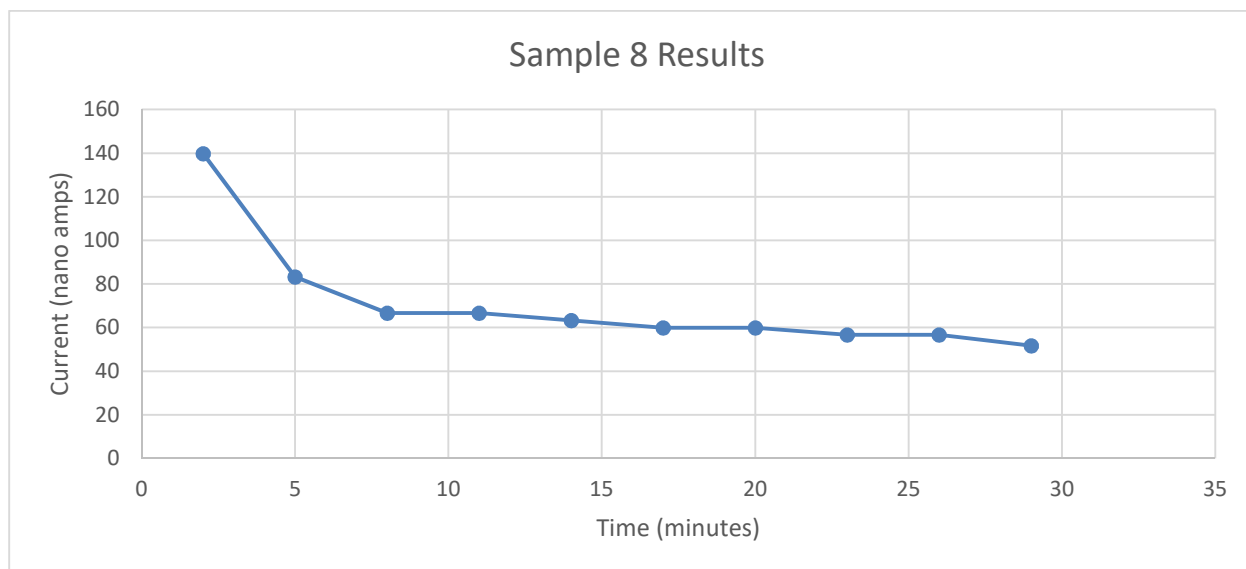
The results for the pure titanium are displayed below (Fig.10). Deposition was carried out for fifteen minutes (Fig 10).



**Figure 10 Sample 6 Results, from Titanium Thin Film**

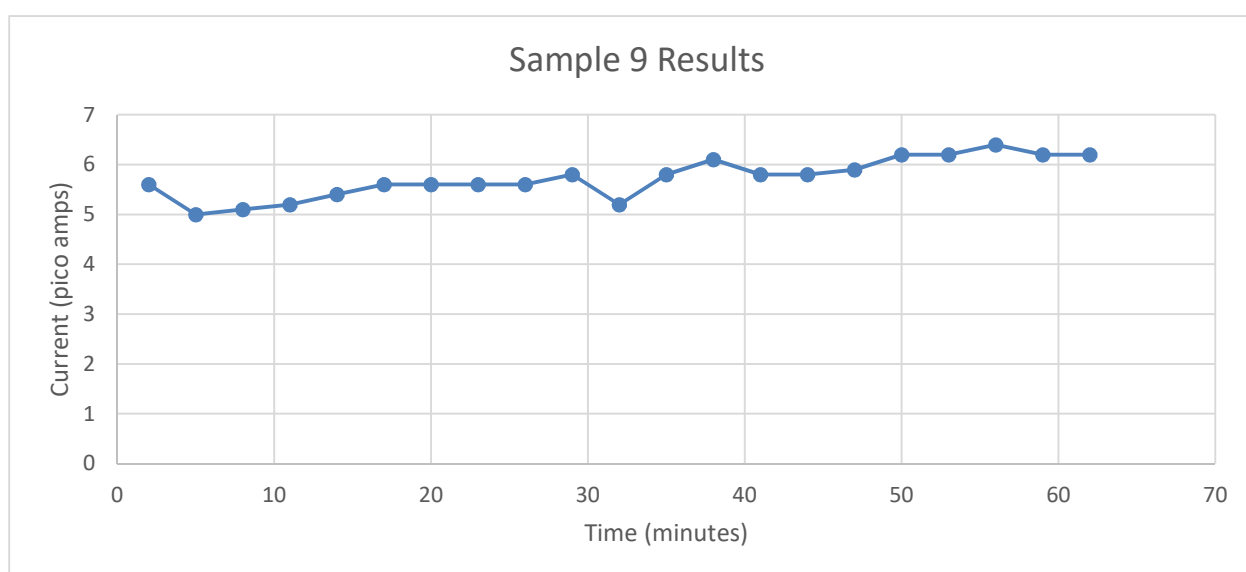
Samples 4 and sample 7 were pure titanium samples, created with a nitrogen atmosphere, but no photoemission was obtained.

The results for aluminium alloy 2060 are displayed below (Fig.11).



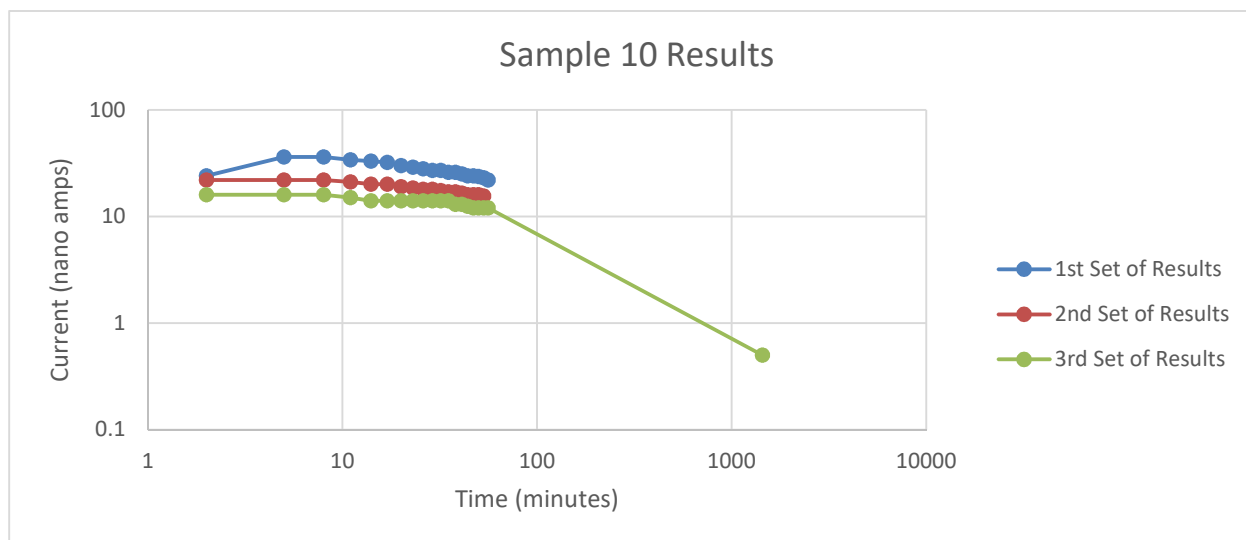
**Figure 11 Sample 8 Results, from Aluminium Alloy 2060 Thin Film**

The results for a two stage experiment are displayed below (Fig 12). The objectives were to create a thin film under very low vacuum for a short time, allow an oxide layer to form and then add a layer of alloy 2060 on top and observe the effect. A film of titanium was created in low vacuum conditions of less than  $10^{-1}$  Torr for two minutes. The system was then depressurised and a film of aluminium alloy 2060 was created at  $10^{-1}$  Torr for five minutes. When taking the last three readings it was observed that the reading did not immediately return to zero when the LED was turned off and lowered slowly from 3 pA (Fig 12).



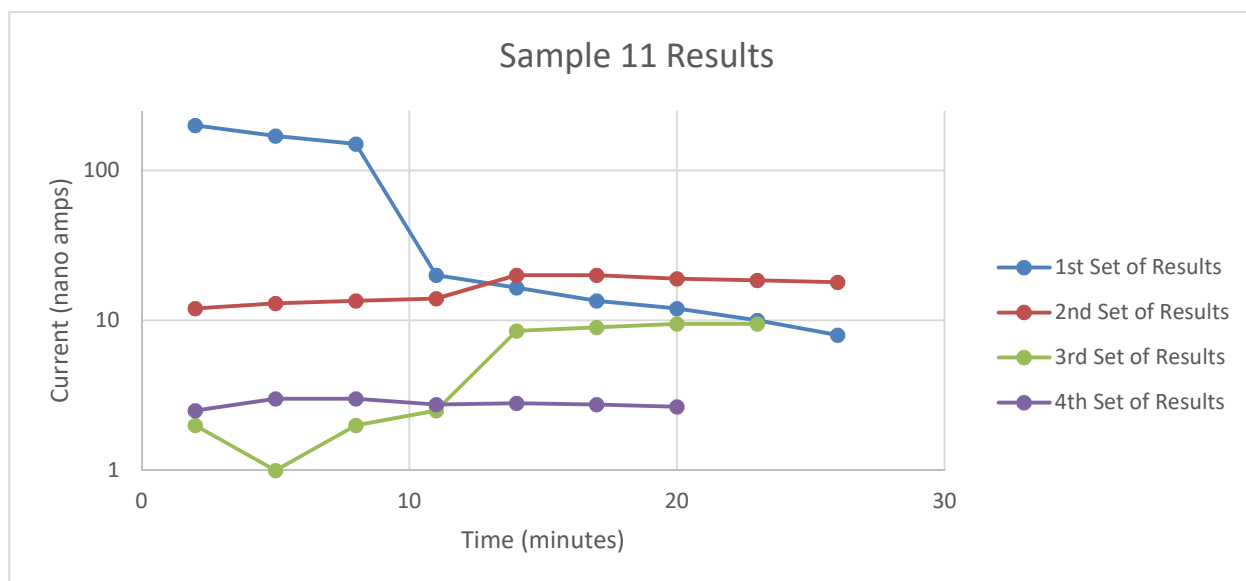
**Figure 12 Sample 9 Results, from Alloy 2060 Deposited over Titanium Film**

Another film of aluminium alloy 2060 was created. The objective for this sample was to see if another high photoemission could be obtained from alloy 2060. Continued to measure the sample after the initial set of readings to see whether the emission rate declined and for how long. There were three sets of readings taken with about an hour spacing between the readings. There was an issue with the first reading of the first set of results. The meter just briefly went straight off the scale and then settled at the value shown. A reading was taken the next day, with all system left running untouched and the value was 0.5 nA (Fig 13).



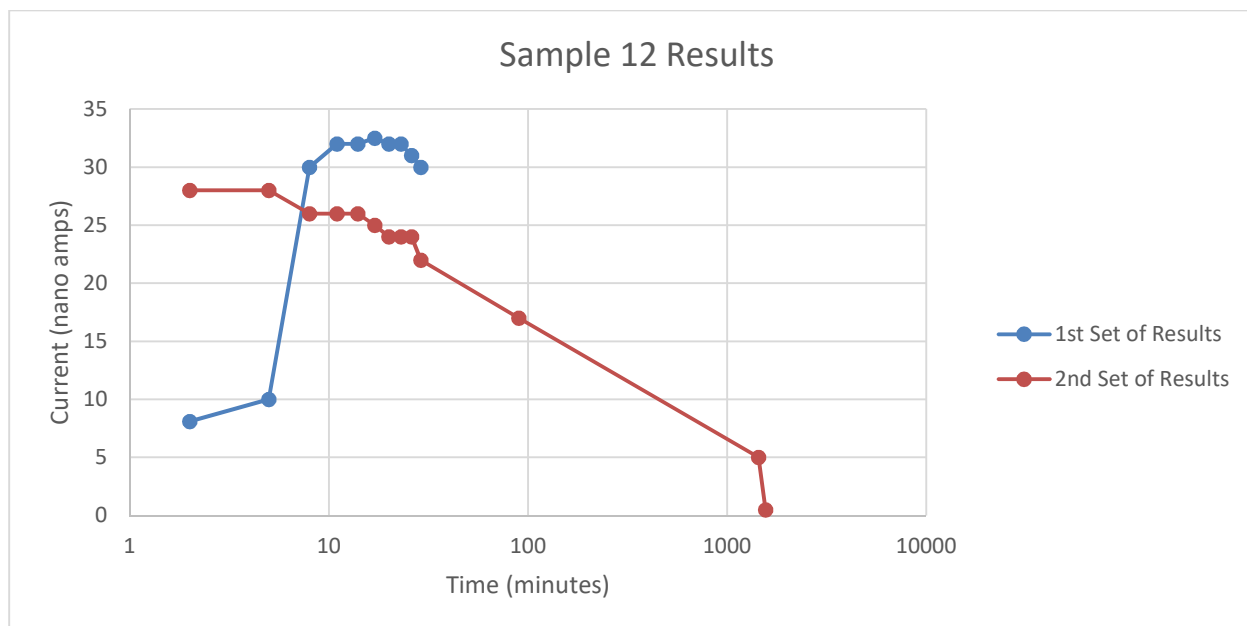
**Figure 13 Sample 10 Results, from Alloy 2060 Film**

The objective of sample 11 was to create a film with alloy 2060 and then introduce air into the chamber and observe the oxidation effect. The first two sets of results were recorded as per the previous experiment. Before the third set of results was observed, the turbo pump was switched off. This meant that the pressure increased from  $10^{-4}$  Torr to  $10^{-1}$  Torr. After 30 minutes, high vacuum was re-established, and the last two sets of results observed. After 24 hours in high vacuum, a final photocurrent reading was taken, but resulted in no photocurrent. Brief instances of reversed polarity were observed across all four sets of results when readings were taken. It is thought that this may be an effect of complicated charged structures, due to layered metal/partially oxidised metal/metal oxide films (Fig 14).



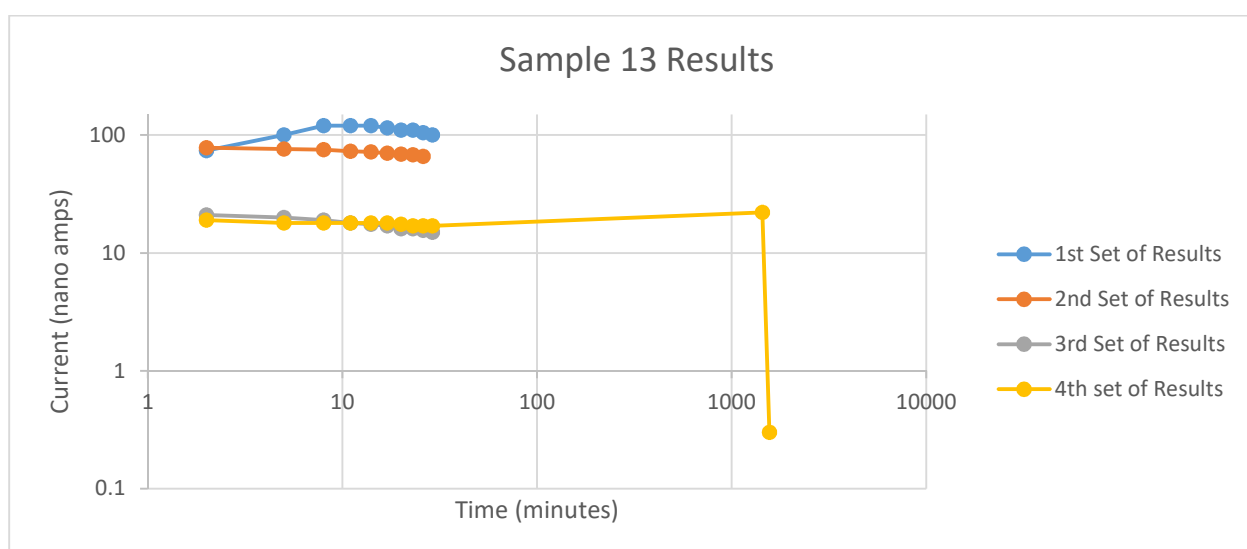
**Figure 14 Sample 11 Results, from Alloy2060, with Air Admission**

Some extra silver was added to the alloy 2060 magnetron target. Conditions were the same as the previous samples. Reversed polarity was observed on the first two readings for approximately 15 seconds. After the first photocurrent measurements had been taken, after 20 minutes, the process was repeated for another set of measurements. After an interval of 1 1/2 hours two readings of 17 nA were recorded. After 24 hours 5 nA was recorded. The chamber was then completely vented to air & then returned to vacuum where a signal of 0.5 nA was recorded (Fig.15).



**Figure 15 Sample 12 Results, from Alloy 2060 Target with Silver Thin Film**

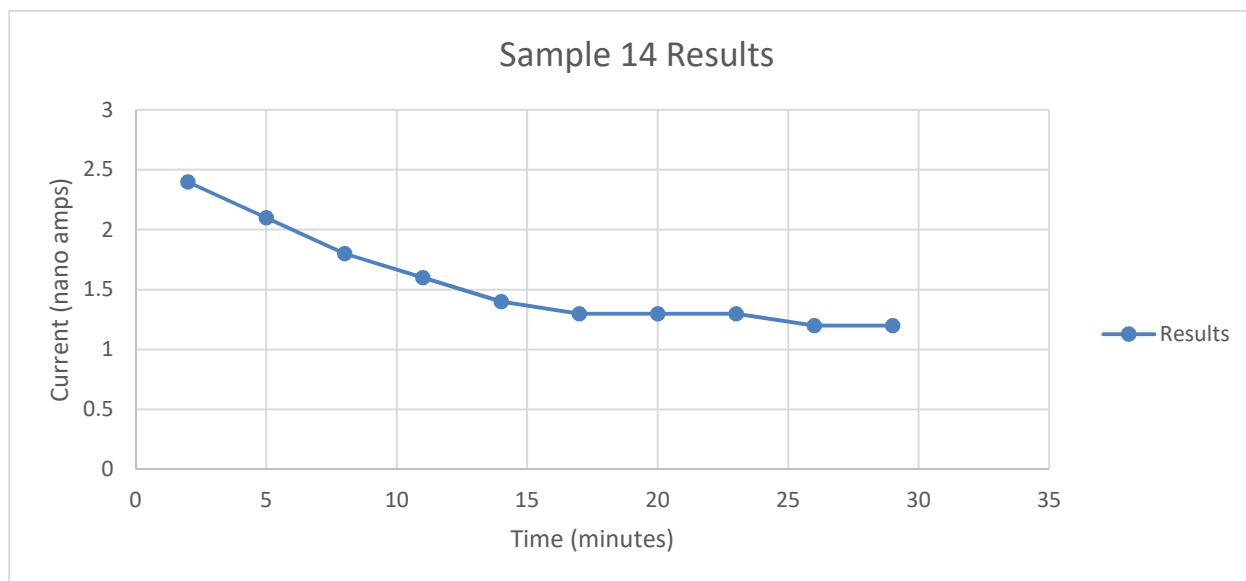
Sample 13 essentially repeats the last two sample tests. After the first two sets of readings, the turbo pump was turned off. High vacuum was restored and the last two sets of readings taken. After 24 hours a reading of 22 nA is taken and the chamber vented to air for two hours before taking a final reading of 0.3 nA (Fig 16).



**Figure 16 Sample 13 Results, from Alloy 2060 with Silver Thin Film**



The final sample 14 was created to check the effect of adding more manganese to alloy 2060. This was achieved by placing manganese powder over half the alloy 2060 sample. Because manganese powder was being used, the cleaning time was extended to 30 minutes. One set of measurements was taken. (Fig 17).



**Figure 17 Sample 14 Results, from Alloy 2060 and Manganese**

### 3.2 Discussion of Results

The experiments had a learning curve in terms of getting the LED working in the chamber in a reliable manner. Also as more samples were created, the more experience was gained. The samples and results are discussed in more detail below.

Sample 1 using alloy 2014 to deposit a film was a short test run to check the equipment was working correctly.

Sample 2 was a successful deposition of alloy 2014 and a consistent set of results was recorded. However the strength of the photoemission current was low and relatively short lived. No more samples of alloy 2014 were created as a result.

Sample 3A deposited a film of titanium successfully, but when the time between readings taken was extended to 10 minutes, anomalies appeared in the data and the rest of this test was devoted understanding why there was an issue. Also found an earthing issue, which was corrected.

Sample 3B was a rerun of the sample and a set of results obtained.

Sample 4 kept the titanium sample, but changed the gas to nitrogen. Deposited a film successfully, but got no readings at all.

Sample 5 was essentially an equipment check, with titanium and argon gas plasma with a full set of readings taken.

Sample 6 repeated samples 3B and sample 5, but it was clear that the strength of the emission was low and short lived due to sample oxidation as can be seen in the results. Because the results were low emission, further samples were not created.

Sample 7 was run as a check on sample 4 and duly returned no current, indicating the film was a material with too high a work function. It was realised a carefully controlled argon nitrogen mix was required for the possibility of a photoelectric emission. However it was not practical in terms of time and alterations to the equipment to do this. Using a nitrogen atmosphere was abandoned.

Sample 8 was the first sample of alloy 2060 created. A very strong photoemission was recorded. The strength of the response was a surprise.

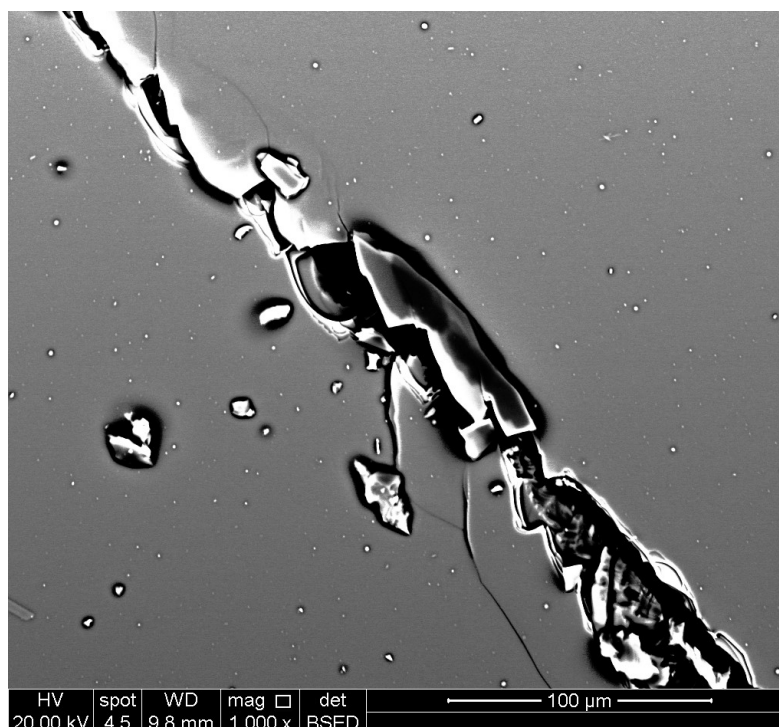
Sample 9 Such a strong response was recorded in sample 8, that is was decided to deposit a very thin film of titanium by only sputtering for two minutes in a very low vacuum of less than  $10^{-1}$  Torr. Then open the chamber and change the sample to alloy 2060, sputter for five minutes and observe the effect. The results recorded were a generally flat curve, but the lowest emission of all the freshly deposited samples. While it was proved that deposition of different materials could be of some advantage, it was not the best way forward and was not pursued.

With sample 10 it was decided to collect more than one set of results to see how the rate of emission declined. Also a reading was taken after 24 hours to check whether there would be an emission after long time oxidation in a low vacuum. From the results obtained the rate of decline looks constant and for the first time a reading was obtained after 24 hours. Very promising set of results.

The sample 11 results after depressurisation were unexpected and tend to confirm what was observed in the previous sample, that the rate of decline appears to be constant. It was expected that the lithium would oxidise first and as a result, drop the current reading very quickly. Again, towards the end of readings there was possible evidence of film charging, as changes in polarity were observed for the first thirty seconds when the LED was switched on.

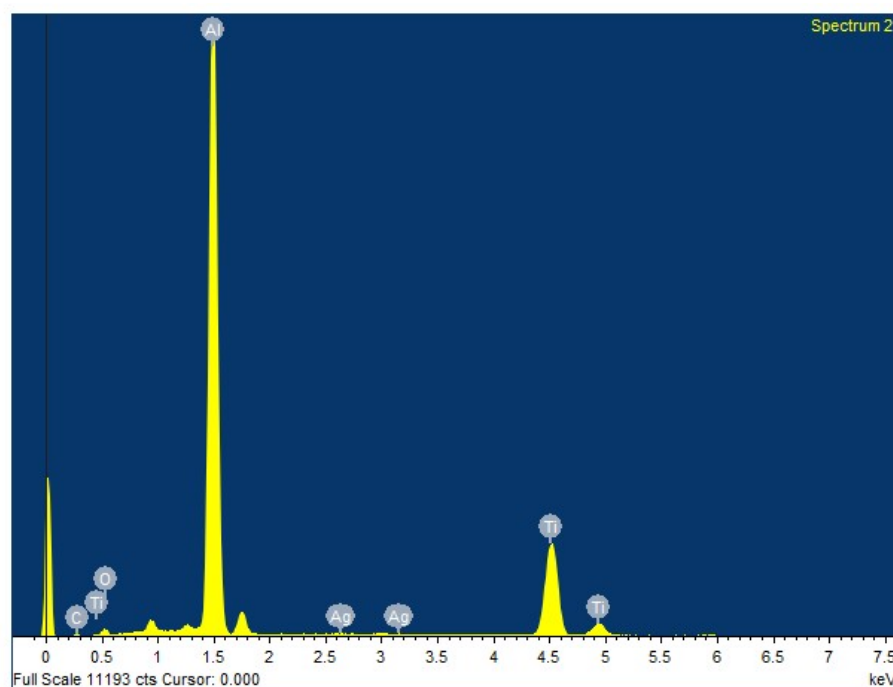
Sample 12 was deposited from Al alloy 2060 plus a small amount of extra silver. The first two readings taken look a little unusual. The second set of readings was taken after 20 minutes. After an interval of 1 1/2 hours a reading of 17 nA was recorded. After 24 hours it was expected that the emission would be zero, but a 5 nA reading was recorded. The chamber was then completely vented to air & then returned to vacuum where a signal of 0.5 nA was recorded. This is the first time a sample has survived for almost 24 hours in vacuum and even after venting to air.

Sample 12 was also examined in the scanning electron microscope and images of the surface taken, along with EDX analysis at 10k eV and also 20k eV (see Fig 18). The image below shows the sample at 1000 magnification and features a crack in the substrate, which was deliberately produced, to see if the structure under the surface would be revealed. Unfortunately, the structure could not be determined around the crack. The EDX results (see Fig. 19) at 10k eV mostly show aluminium, very little silver and not any lithium or copper (the alloy elements). There was a considerable amount of oxygen on the surface. Detailed analysis is beyond the scope of this work. A test at 20k eV did show silicon. This indicates that the sample (thin film) has thickness just above 1 micron, which is enough for photoemission production. Again, the lithium could be obscured by the surface oxygen. The artefacts (white dots) on the surface were examined and most appeared to be possibly silver particles. It was impossible to get conclusive quantification results from them as they a bit too small for EDX analysis. The overall quantification results are presented at the Table 4.



**Figure 18 Backscatter image of sample 12, 1000 Magnification**

A significant amount of carbon can also be seen. Probably contamination on the sample from handling and possibly pump oil from the vacuum pump. The oxygen content is not surprising, and it is most likely concentrated very near the surface. Further detailed analysis will be done in the future.



**Figure 19 EDX Spectra of Sample 12, 10 keV Electron Beam**

**Table 4 Elemental Content of Sample 12, 10 keV Electron Beam**

Element	Atomic%
C	18.22
O	9.04
Al	51.32
Ti	21.22
Ag	0.21
Totals	100.00

Sample 13 used the same alloy and silver sample and was a combination of samples 11 and 12. As recorded in the results, the turbo pump was turned off after the first two sets of observations and the effect of oxidation observed in the third set of results. The third and fourth sets of results were observed after the turbo pump was turned back on and left running overnight. A surprisingly strong signal of 22 nA was recorded the next day. The chamber was vented to and kept at air for 2 hours. A photoemission signal of 0.3 nA was recorded. This was by far the most successful sample.

Sample 14 was a deposition of 50% manganese powder and alloy 2060, to check the effect of adding more manganese to the alloy. The results recorded were low emission and not pursued.

## Chapter 4 Conclusions and Recommendations

### 4.1. Conclusions

It is almost universally perceived that oxides have a very high work function and it will be impossible to have photoemission from oxides in low vacuum, when oxidisation takes place under near ultra-violet light. The results of this study shows that it is possible to find material combinations to partially overcome adverse oxidisation influence on the quantum yield at excitation energies of around 4 eV. Some materials in the form of thin films, produced a workable photo response under LED UV light even after significant exposure to low vacuum and even a short period of oxidation in air.

From the results the following conclusions were derived.

1. Some materials which promised reasonable photoemission response such as titanium sample #6, alloy 2014 sample #2, and manganese (added to alloy 2060), sample #14 had not produced satisfying results, so work on these materials was not developed further.
2. The switch to explore nitrides with samples #4 and #7 was not successful. As with the other low performing samples, the work on nitrides was not pursued further.
3. The approach of using an alloy with a low work function element, such a lithium, produced good results, with sample #13 being the best long term photoemission readings obtained.
4. The additional silver added to the alloy appears to have had the effect of stabilising the photoemission.

### 4.2 Recommendations

Photoemission in low vacuum has not been the subject of much research anywhere so far. There is no developed base of knowledge to build further on. The MSc was very challenging, and involved modifying an experimental system, training in experimental techniques and establishing experimental procedures. The results have only outlined and signposted further possibilities, and so cannot answer many questions. From this point of view :

1. From the results with alloy 2060, this approach looks promising as the concept of alloying a low work function element has produced good results. Further work with alloy 2060, increasing the amount of silver looks like an area to explore.
2. Combining two or more thin films as per sample #9 would also be an interesting experiment. Two or more films of differing properties could be deposited. The objective would be to produce a surface with strong photoemission and longevity in a low vacuum environment. The approach has the potential to produce more stable emitters.
3. As mentioned above, magnetron sputtering can be used to create alloy films of any combination within the limitations of the equipment. Taking the experience gained from using standard commercial alloys and pure elements such as silver, there is a possibility to create a custom alloy which is not readily commercially available.

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## Appendices

### Appendix 1 Tabular Comparison of Aluminium Alloys 2014 and 2060

<b>Alloy 2014</b> - Source Matweb materials website													
	<b>Al</b>	<b>Si</b>	<b>Fe</b>	<b>Cu</b>	<b>`</b>	<b>Mg</b>	<b>Zn</b>	<b>Ti</b>	<b>Cr</b>			<b>Other Each</b>	<b>Other Total</b>
Max	BAL	1.2	0.7	5	1.2	0.8	0.3	0.2	0.1			0.05	0.15
Min		0.5		3.9	0.4	0.2							
<b>Alloy 2060</b> - Source Supplier Certified Material Inspection Report													
	<b>Al</b>	<b>Si</b>	<b>Fe</b>	<b>Cu</b>	<b>Mn</b>	<b>Mg</b>	<b>Zn</b>	<b>Ti</b>	<b>Ag</b>	<b>Li</b>	<b>Zr</b>	<b>Other Each</b>	<b>Other Total</b>
Max	BAL	0.1	0.1	4.5	0.5	1.1	0.5	0.1	0.5	0.9	0.2	0.05	0.15
Min				3.4	0.1	0.6	0.3		0.1	0.6	0.1		

# Appendix 2 Aluminium 2060 Material Certificate

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## CERTIFIED INSPECTION REPORT

We hereby certify that the material covered by this certificate has been inspected with, and has been found to meet the applicable requirements described therein, including any specifications forming a part of the description and that samples representative of the material met the composition limits and had the mechanical properties shown on the face of this sheet. This test report shall not be reproduced except in full, without the written approval of the Quality Department. No alteration, addition or other change is authorized to be made to this certificate. The recording of false, fictitious, or otherwise fraudulent statements or entries on this certificate by any recipient may be punished as a felony under applicable law.

*Rob Woodall*

Rob Woodall  
Director of Manufacturing Davenport Works

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Customer: Arconic Item  
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SMITHS ADVANCED ME 6041170188R01

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Page 2 of 2

Lot: 721675 - Mechanical, Physical, Metallography, Quantometer Results (cont.)

Notes for Lot: 721675

Customer accepted failing FCG on deviation, per 2014/07/22 letter signed by Greg Venema and Li Hong Ping.

Lot: 721675 - Mechanical, Physical, Metallography, Quantometer Results

Temp	Dir	Test	UTS	KSI	PCT	TVS	ELAD
T8E30	Longitudinal	4	76.1	88.9	13.4		
			75.2	86.7	11.1		
			75.8	86.9	12.7		
			75.6	87.8	13		
T8E30	Long Transv.	4	72.5	82.3	15.7		
			73.5	83.3	15.9		
			73	82.8	15.4		
			73.4	82.7	15.3		

Temp Dir  
T8E30 T-L Max  
Min 114.7

T8E30 Exfoliation Corrosion PASS  
Cast Number Chemical - OES SI FE CU MN MG ZN TI AG LI ZR Other Each Other Total  
8557843 Actuals 0.02 0.02 3.7 0.29 0.8 0.35 0.03 0.33 0.8 0.11 < 0.05 < 0.15

This material was melted in the United States or a Qualifying Country [REF DEAPS 225-872.1(a)]; it was manufactured in the United States